PERFORMANCE OF SELF-DECONTAMINATING TEXTILES FOR CHEMICAL PROTECTIVE CLOTHING

A Thesis

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ABSTRACT

The objectives of this study are to develop an experimental system appropriate for studying chemical protection by the mechanism of destructive adsorption with these self-decontaminating surface treatments applied to traditional porous textiles and to determine whether the addition of these features will add significant protection from dermal pesticide contamination. A test procedure for chemical protective clothing fabrics was evaluated to focus on chemical protection by the mechanism of adsorption on conventional woven fabrics treated with two self-decontaminating textile treatments, N-halamine and MgO nanoparticles. Both treatments demonstrated some degree of degradation of the pesticide aldicarb. However, the MgO treated samples achieved farther degradation than the N-halamine. These types of materials have potential for enhancing chemical protection and comfort given relatively low volume contamination conditions as modeled in this experiment.

BIOGRAPHICAL SKETCH

Ellan, daughter of Betty and Richard Spero grew up in Stony Brook, New York. She received a B.S. (2003) in Fiber Science from Cornell University. and M.A. (2008) from The Fashion Institute of Technology in Fashion and Textile Studies: History, Theory and Museum Practice.

ACKNOWLEDGEMENTS

This document represents a small fraction of what I have learned upon returning to this university on the hill. Ever since my first conversation with Kay Obendorf when she encouraged me to come to Cornell as an undergraduate, she has continued to be a brilliant mentor and friend. I am honored to be one of her students and a small part of her legacy in the field of textiles. The giants whose shoulders I stand upon are first of all my parents, whose individuality, encouragement and sacrifice taught me to live without boundaries.

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CHAPTER ONE: INTRODUCTION

1.1 Pesticide Use in the Agricultural Environment

Pesticides play a major role in food production and public health, both in maintaining crop abundance and limiting the spread of disease via animal or insect carriers. However, human occupational exposure as well as environmental contamination through soil and groundwater can have serious effects. This group of chemicals includes "(a) any substance or mixture of substances intended for preventing, destroying, repelling or mitigating any pest, and (b) any substance or mixture of substances intended for use as a plant growth regulator, defoliant or desiccant (Krieger et al. 2007). In the agricultural environment, chemicals are employed in liquid and granular forms and vary greatly in quantity used and toxicity.

Pesticide use continues at high levels on a global scale. A report from the U.S. Environmental Protection Agency shows world pesticide use at over 5.0 billion pounds of formulated pesticide (a mixture of active ingredient and other inert substances) in 2000 and 2001, with the United States accounting for nearly one quarter of total usage (Kiely et al. 2004). According to the National Pesticide Use Database for 1997 to 2004, in the U.S. pounds of active ingredient of pesticide used to control insects applied per year averaged 158 million (Gianessi and Reigner 2006).

1.2 Human Pesticide Exposure

Chemicals may enter the body through a variety of routes including ingestion on food or in drinking water, inhalation, and absorption through the skin. Although food safety issues have gained high visibility, occupational exposure for people involved with mixing, loading or application of pesticides is also a major health issue (Krieger et al. 2007). Dermal absorption, rather than inhalation or ingestion is the primary route for occupational chemical exposure (Wolfe et al. 1967).

Pesticide exposure levels are influenced by a variety of factors such as wind, type of activity, method and rate of application, duration of exposure, and worker hygiene (Wolfe et al. 1967). Distribution patterns on worker's garments vary with method of application, equipment used and environmental conditions. Research has often focused on contamination caused by spraying. Studies of garments after pesticide application with air blast sprayers showed a general trend of higher exposure levels on the upper body (forearm, shoulder, chest, neck) rather than the lower body (Koh and Obendorf 1993, DeJonge et al. 1985) found the highest concentration of sprayed chemicals on arms, head, and back upper torso. Coffman et al. (1999) observed the highest concentration on the neck, upper arm and shoulder in a diagonal pattern from upper right shoulder (spraying arm) to lower left torso. The use of a hooded sprayer with high volume, low concentration output produced considerably less contamination than an air-assist sprayer. Nigg et al. (1990) found higher deposition on the thigh rather than chest when a canopied tractor was used to pull the air blast sprayer. These non-uniform distribution patterns highlight the difficulty in identifying body regions in

need of specified protection and associated design challenges for individual circumstances.

Aldicarb, the pesticide used in this study is produced commercially in granular form, which is applied to the subsoil. This is a safety precaution to reduce handling hazards associated with spraying aqueous chemicals. Often the most hazardous pesticides are produced in this type of formulation because it is considered to result in potentially less human exposure. Water is needed to release the active ingredient. However, studies have shown a potential for dermal pesticide exposure from granular formulations when these soils are trapped in garment folds or pockets. Moisture and oily secretions associated with sweating can also affect transfer of granular pesticide to skin (Nelson et al. 1993). Although moisture may have a diluting-effect on water-soluble chemicals, it can also promote permeation through the skin (Scheuplein and Blank 1971).

1.3 Health Effects

Despite difficulty in measuring and predicting long-term exposure effects in humans, a wide variety of health hazards related to common pesticides are known. Local effects of pesticides include irritation, allergic contact dermatitis, photoirritation, photoallergic contact dermatitis, contact urticaria and subjective irritation. Systemic effects include seizures, aplastic anemia, various neurological symptoms, cognitive and psychomotor dysfunction, sterility and some rare fatalities (Tripp et al. 2007, Kamel and Hoppin 2004).

Cases of aldicarb poisoning, both accidental and occupational, involve reaction with cholinesterase enzymes, specifically interference with the hydrolysis of acetylcholine which impacts neural transmission (Carpenter and Smyth 1965, Weil and Carpenter 1968 a,b,c, Dorough 1970, World Health Organization 1991). Clinical symptoms observed in humans vary with exposure and may include: dizziness, salivation, excessive sweating, nausea, epigastric cramps, vomiting, diarrhea, bronchial secretion, blurred vision, non-reactive contracted pupils, dyspnoea, and involuntary muscular contractions. Exposure cases have been treated successfully with atrophine (World Health Organization 1991).

1.4 Mitigation Strategies

Agencies such as the Environmental Protection Agency (EPA), United States Department of Agriculture (USDA) and California Department of Pesticide Regulation (CDPR) develop mitigation strategy systems to reduce occupational pesticide exposure. Although specific guidelines vary with individual chemicals and situations, these measures combine several closely related approaches to create practical and enforceable procedural modifications. General criteria include: use of personal protective equipment (PPE), engineering controls, limit of exposure time or reduction of active ingredient, and establishment of buffer zones. Garment materials can range from highly specialized protective suits to conventional woven cotton/polyester work clothing, typically including: coveralls, aprons, respirators, gloves, footwear, protective eyewear and headgear. In general their protective properties are derived from barrier, repellency, adsorption, or

a combination of these mechanisms (discussed in Chapter 2.2).

The use of PPE may seem like a simple solution to directly limit exposure. However, many factors such as proper usage and selection, decontamination or disposal of pesticide exposed clothing, material type, garment comfort and appropriate fit impact effectiveness of protective clothing systems. Clothing that limits pesticide exposure may also limit water vapor transmission and contribute to discomfort or heat stress. Workers may misuse more occlusive garments by not closing them properly to allow for increased ventilation and inadvertently decrease their personal protection. For these reasons, workers may prefer more traditional types of garments such as denim coveralls.

Engineering controls such as closed mixing/loading systems, mechanical harvesting, enclosed cab with filtration for vehicles and water-soluble packaging can reduce the need for certain PPE and promote a more comfortable working environment when used properly. However, despite the possible benefits afforded by combining PPE and engineering controls many workers are confused about the interactions between these protective approaches. Coffman emphasizes the need for a multidisciplinary approach including material, system and educational improvements to protect workers from occupational pesticide exposure (Coffman 2009).

Effectiveness of any protective garment or engineering control system is dependent on proper usage. This includes successful decontamination, often achieved through laundering. However, over time fabric properties and effectiveness may change (Laughlin 1994). Even properly used, garments may still contaminate the wearer during doffing. Thus, it may be useful to employ textile treatments that reduce the toxicity of contaminants through oxidation

or destructive adsorption. These self-decontaminating properties could reduce the toxicity of chemicals before the laundering process.

1.5 Objectives

The research presented in the following paper focuses on a class of conventional woven fabrics with self-decontamination properties and their potential application for use in protective garments. Textile treatments contained N-halamine, magnesium oxide nanoparticles, and starch on plain woven cotton/polyester fabrics compared to an untreated control fabric. The objectives of this study are to develop an experimental system appropriate for studying chemical protection by the mechanism of destructive adsorption with these self-decontaminating surface treatments applied to traditional porous textiles and to determine whether the addition of these features will add significant protection from dermal pesticide contamination.

CHAPTER TWO: REVIEW OF LITERATURE

2.1 Chemical Protective Clothing Systems

Basic personal protective equipment (PPE) for which there are U.S. Environmental Protection Agency (EPA) guidelines includes: coveralls, apron, broad-brimmed waterproof hat, boots, rubber gloves, goggles or face shields. These pieces are constructed of a variety of material types from highly specialized selectively permeable membranes to everyday clothing fabrics such as denim. They can be disposable or reusable, each with benefits and drawbacks depending on the situation, working environment, user groups and toxicity of the pesticide that govern the choice of PPE. The Center for Disease Control and Prevention (CDC) recommends that people working as mixers, loaders and applicators of pesticides wear protective clothing according to the EPA guidelines (CDC 2005). However, specific PPE choices are ultimately left to the end user. New performance specifications for chemical protective body garments are under development by the American Society for Testing and Materials (ASTM) and the International Organization for Standardization (ISO) (ASTM 2006). In the existing standards, materials are categorized into three different levels based on average penetration values for a given challenge chemical. Properties included in the scheme include; material and seam resistance to penetration by liquid under pressure, resistance to permeation (in the absence of applied pressure), breaking and tearing strength.

The selection of PPE is a compromise between protection and comfort levels in addition to cost. Of course, the ideal system would provide high

degrees of comfort and protection at an affordable cost. However, there is no one overall optimal ensemble.

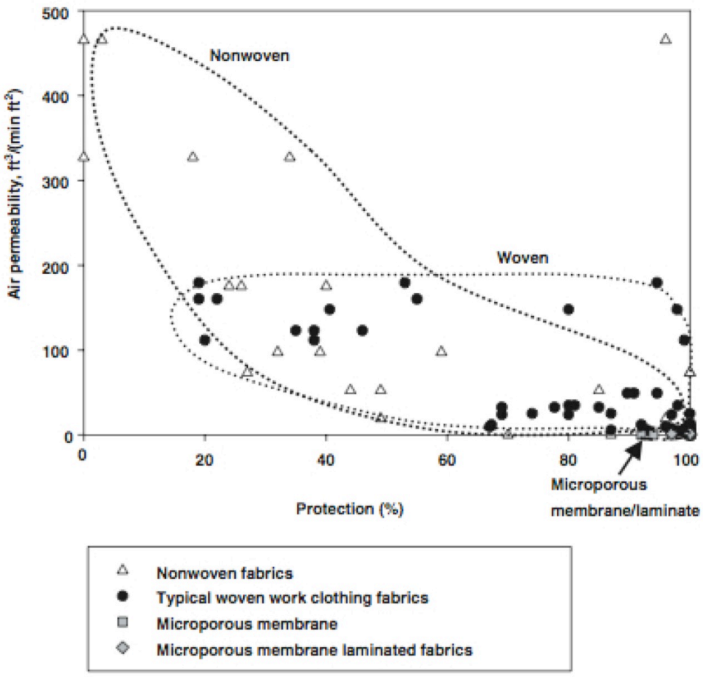


Figure 2.1 Relationship between protection and permeability for nonwoven, woven, microporous membranes and laminates (Lee and Obendorf 2007)

Protective garments function primarily by barrier (no permeation or penetration), repellency, adsorption or a combination of these mechanisms. Thus, chemicals are kept away from the skin by retention in the fabric structure or rolling off the outside layer without penetration. In Figure 2.1, Lee and Obendorf (2007) show the relationship between protective properties and air permeability for materials including typical woven work fabrics, nonwovens, microporous membranes and laminated fabrics. A simplified concept of these relationships (Figure 2.2, Lee and Obendorf 2007) shows the common range of protective materials and their general comfort and

performance characteristics. The nonwovens have the largest range of pore spaces, and thus comfort properties due to air permeability. The ideal fabric, which optimizes both comfort and protective properties is outside of the rage of currently available materials.

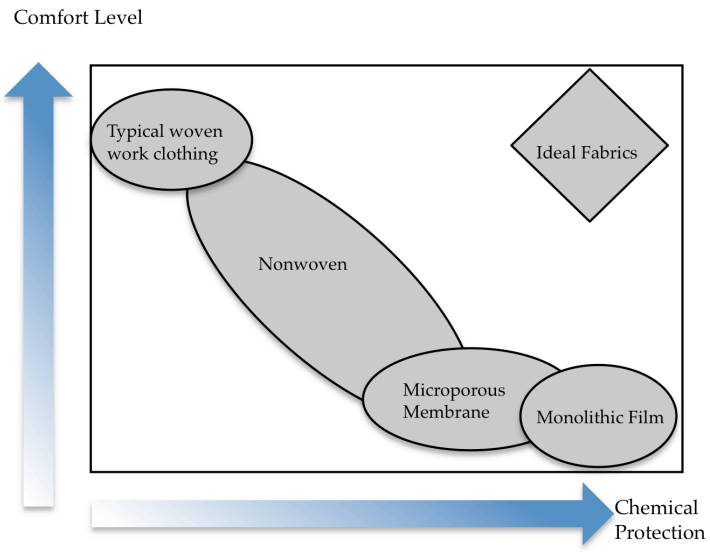


Figure 2.2 Protection/Comfort model for PPE (Lee and Obendorf 2007)

Performance of typical woven work clothing can be enhanced with the addition of finishes such as flourocarbons (Laughlin et al. 1986) or starch (Obendorf et al. 1991, Csiszar et al. 1998). The category of nonwovens demonstrates a large range of properties since they can have a wide distribution of pore sizes. Monolithic films have the greatest degree of protection since they act as impermeable barriers. Microporous membranes, in comparison have increased comfort due to the presence of pores, which allow for water vapor transmission. The ideal fabric maximizes both comfort and protection by combining these mechanisms (Lee and Obendorf 2007).

These protective properties are governed by both chemical and structural material characteristics.

2.2 Materials and Mechanisms for Chemical Protection

Textile weaving creates a highly-complex three-dimensional lattice with overall material properties derived from a combination of fiber chemistry and geometry, degree of open spaces, and tightness in yarn and weave structure. Pesticide penetration is governed by properties of the material (content and structure) as well as challenge chemical. Materials used for protective clothing should balance barrier properties against harmful chemicals with some permeability for air and moisture transport to maintain comfort. Contamination may occur through a combination of permeation, penetration, and absorption. Structural and chemical characteristics of the material determine which mechanism will dominate when exposed to a liquid challenge chemical. In porous media such as textiles, bulk liquid flow through the openings in the material is the primary mechanism for penetration of chemicals (Lee and Obendorf 2007). For monolithic materials (often used for gloves), permeation occurs primarily via absorption, diffusion, and desorption of molecules.

2.2.1 Barriers to Permeation

Some protective garments, such as gloves, act primarily as barriers to chemical permeation. This is a process of molecular diffusion through a solid material, which governs the contamination of skin or monolithic barrier

materials such as glove films or coatings. Permeation involves the sequential absorption of molecules, diffusion of absorbed molecules followed by desorption into a collector material. From Fick's Second Law, the diffusion rate of a given chemical through a material is proportional to the concentration difference through the material:

$$d\phi/dt = D\, d^2\phi/dx^2 \qquad (2.1)$$

ϕ = concentration

t = time

D = diffusion coefficient

x = diffusion distance.

Chemically-resistant gloves or suits designed for high levels of exposure are commonly made from this type of monolithic film or use a film or coating as part of a system. Common materials for reusable suits and gloves include: butyl rubber, nitrile, neoprene and chlorinated polyethylene. Disposable garments are often made from non-woven polyethylene (PE, Tyvek) which can also be laminated to other materials (Raheel 1994).

Since monolithic barrier materials do not have a porous structure; air and moisture permeability are limited; liquid challenge chemicals are generally repelled in the absence of high pressures. Contamination for these materials is primarily achieved by absorption, diffusion, and desorption. In these cases, since flow through the material is negligible, liquid chemicals, vapor and moisture remain contained on either side of the barrier. In the case of glove materials, the type of carrier solvent and concentration are the primary factors to impact permeation of the active ingredient. There were no

universally effective glove barrier materials against active ingredients in solvents such as alcohols, ketones, aliphatic and aromatic petroleum distillates. However, in general nitrile, butyl and Silver Shield® materials were more effective than polyvinyl chloride and natural rubber (Schwope et al. 1992, Schwope 1986).

Although effective barriers to pesticide penetration for tasks with high risk of spilling or large volume contamination, full-body chemical suits can limit water vapor transport causing heat stress and fatigue, unless a cooling device is included. Thus, they are often inappropriate for extended use in outdoors at elevated temperatures. In California agriculture, full-body chemical resistant suits are not permitted at temperatures exceeding 80°F during the day (85°F night) (Thongsinthusak and Frank 2007).

2.2.2 Adsorbency and Liquid Penetration for Porous Materials

The way that a textile surface interacts with a liquid challenge chemical is governed by physical characteristics of the materials. This is dependent on the chemical nature, surface configuration and fiber roughness, pore geometry of the textile, and liquid parameters such as surface tension and viscosity. In order to discuss the penetration of pesticides through protective materials, it is necessary to understand the mechanisms of interaction between challenge liquids and textile surfaces. The processes of surface wetting and wicking form an important foundation for understanding the two major mechanisms for protective clothing materials, adsorbency and repellency.

Penetration into or through the fabric can only occur if the material is "wettable." In wetting, the fiber-air interface is displaced by a fiber-liquid

interface. Spontaneous wetting is the flow of a liquid over a solid surface toward thermodynamic equilibrium in the absence of external forces. The displacement of a fiber-air interface with a fiber-liquid interface is characterized by the contact angle (Θ) formed between the liquid and solid and their surface energies. The Young-Dupré equation (Kissa 1996) describes this equilibrium at the solid-liquid interface:

Young-Dupré equation:

$$\gamma_{SV} - \gamma_{SL} = \gamma_{SV} \cos\Theta \qquad (2.2)$$

γ = interfacial tension;

S, L, V denote solid liquid and vapor phases;

Θ = equilibrium contact angle.

Wettability increases with decreasing contact angle as cos Θ increases. Total wetting implies that Θ approaches zero, cos Θ approaches 1. At the maximum value for cos Θ is the critical surface tension of a solid (γ_c), a constant property of a given solid. Thus, spontaneous spreading and wetting only occurs when the liquid surface tension is less than or equal to the critical surface tension of the solid. If wetting does occur, capillary force-driven wicking also allows the flow of liquid through a porous material (Lee and Obendorf 2005, Hsieh 1995, Kissa 1996, Miller 1977).

After wetting of fibers assembled with capillary spaces between them occurs, capillary forces drive the spontaneous flow of the liquid through the porous substrate, in the wicking process. Pesticide penetration is defined as the flow of a chemical through pores, or other discontinuities in the material such as closures or other imperfections. The flow of a liquid through a fibrous

material may be described using a capillary bundle model with the Laplace and Poiseuille equations (Lee 2000, Miller 1998) to describe penetration and flow through respectively:

Laplace equation:

$$P = \frac{2\gamma \cos\Theta}{r} \qquad (2.3)$$

Poiseuille equation:

$$Q = \frac{\pi r^4}{8\eta} \cdot \frac{dP}{dl} \qquad (2.4)$$

l = pore length

r = pore radius

γ= liquid surface tension

Θ = solid/liquid contact angle

η = viscosity

P = pressure

Q = liquid flow rate

As described by the Laplace equation, positive capillary pressure (and thus liquid flow) occurs when cos Θ is positive, the contact angle is between 0 and 90 degrees. The Poiseulle equation shows the inverse relationship between the flow rate in a tube (capillary) and the distance that the liquid travels (Kissa 1996).

Porosity (φ), the fraction of void space in a porous medium:

$$\varphi = \frac{1 - \rho_b}{\rho_s} \qquad (2.5)$$

ρ_b = fabric density

ρ_s = fiber density

is an important material property for adsorbency, flow of liquids and vapor transmission. Fabric density can be calculated by:

$$\rho_b = \frac{\text{fabric weight } (g/m^2)}{\text{thickness (m)}} \qquad (2.6)$$

Both liquid and fiber density factor into determining the maximum adsorption capacity (C_m):

$$C_m = \frac{\rho_l}{\rho_s} \cdot \frac{\phi}{1-\phi} \qquad (2.7)$$

ρ_l = liquid density
ρ_s = fiber density
ϕ = fraction of volume made up of pores (void).

Adsorption is governed by inter and intra-fiber spaces where liquids are retained through capillary forces. When fabrics have the same weave structure, yet different fiber contents, the adsorption capacity can be also quite different due to different fiber pore structures. Pore geometry and connectivity however is not easily described (Hsieh 1995). Pore sizes for woven fabrics commonly have a bimodal distribution. Large sizes represent the inter yarn spaces, whereas the interfiber spaces are reflected by smaller spaces (Miller and Tyomkin 1994, Lee and Obendorf 2005). For woven

(Tencel) and nonwoven (polyethylene) fabrics with similar solid volume fraction (0.386, 0.399 respectively), Lee and Obendorf (2007) observed different water vapor transmission rates (20 and 15 g/(hm^2)) and through pore size distributions. The woven fabric showed a range of pore diameters of 6.5 – 114.4 μm, whereas the nonwoven ranged from 0.3 – 6.2 μm, all pores smaller than the lower bound of the woven distribution. They demonstrated that a property such as water vapor transmission rate cannot be linked solely to a characteristic such as solid volume fraction but may also include pore size and fiber hydrophobicity.

Researchers have created statistical models to predict qualities of comfort and protection based on basic physical properties of fabrics and challenge liquids (Lee and Obendorf 2001, 2005, Zhang and Raheel 2003). Pore size and fiber type, in conjunction with chemical factors such as formulation, solvent and viscosity determine the degree of possible penetration. Material properties which impact the capillary size and shape such as yarn/fiber and weave type, chemistry and applied finishes impact liquid chemical penetration in a porous textile material. Air permeability is also associated with structure. In general, an open porous loosely-woven structure will permit penetration by air and liquid challenges. Fabric cover factor, describes the degree of compactness of weaving, or interyarn space. Twist factor represents the "hardness" of a yarn and is also a measure of compactness between yarns of comparable size. Lee and Obendorf (2005) found a negative relationship between cover factor, fabric thickness, and twist factor with penetration.

2.3.3 Strategies for Improving the Protective Properties of Porous Textiles

Enhanced Repellency

A fabric that displays repellency has a critical surface tension that is lower than that of the liquid, creating a bead on the surface, which can roll off rather than penetrate the internal fabric structure. Finishes such as fluorocarbons may be applied to fabric surfaces to alter the surface tension and wetting characteristics. In a study of nonwoven chemical protective fabrics, Lee and Obendorf (2001) found that the difference in surface tension between the fabric and challenge liquid had the highest correlation with pesticide penetration, followed by solid volume fraction, fabric thickness and viscosity. The interaction between the fiber-liquid interface is described by the Young-Dupré equation (2.2). Fabrics with repellent finishes have low surface energies and function by repellency independent of fiber type or fabric porosity. Untreated fabrics however, function by a combination of repellency, wicking and adsorbency which take into account not only liquid-medium surface interaction but also other characteristics of the liquid and fabric. Lee and Obendorf (2001) identified an empirical diverging point for surface tension difference (γ_S-γ_L) at -13 mN/m, separating those materials which function solely by repellency (γ_S is small) from those governed by a combination of mechanisms.

Enhanced Adsorbency

Many textile structures have the ability to retain liquids and other chemicals via adsorption. This property may provide protection by trapping a contaminant within a fibrous matrix limiting dermal contact. This is the

mechanism of activated carbon, which is used in military garments. Washable woven garments made from cotton often blended with other fibers such as polyester are popular garments for pesticide applicators, especially those working in hot environments. This traditional work clothing functions by adsorption and has demonstrated a reduction in dermal pesticide exposure (Welch and Obendorf 1997, Obendorf et al. 2003). Many agricultural workers prefer traditional work clothing with its comfort, cost, and availability (DeJonge et al. 1985). These materials however provide a generally lower level of protection than specialized barriers or selective membranes due to their higher degree of porosity and large pore sizes.

Although the National Institute for Occupational Safety and Health (NIOSH) reports that work clothing such as long-sleeved shirts and long pants can provide 90% protection, dermal pesticide exposure even on a comparatively small-scale can have dramatic health effects (Thongsinthusak and Frank 2007). It is reasonable to treat this as a baseline for minimum protection subject to continual improvement. Traditional fabrics act primarily as an adsorptive barrier to limit chemical exposure, by the retention of contaminants within the fabric structure.

Researchers have shown that treatment of traditional non-barrier textiles with chemical finishes which increase sorption properties such as starch can both decrease transfer by rubbing and enhance removal of contaminants by laundering (Obendorf and Solbrig 1986, Koh et al. 1993, Obendorf and Ko 1997). When thickness increases, there is greater chance for liquids to be trapped within the fabric structure, rather than finding well-aligned and open paths to flow through. Following this reasoning, layering of clothing materials has been shown to offer increased protection (Laughlin et

al. 1986, Crossmore and Obendorf 1992). Adsorbency combined with decontamination is the major mechanism for protection, which is studied in the experiments described in the following sections.

Selective Permeability

Another approach to achieving a balance between chemical protection and comfort is limiting pore size. Selectively microporous membranes, which allow air penetration but prevent liquid penetration, may alleviate the thermal discomfort often associated with traditional barrier materials while maintaining a high degree of chemical protection. When laminated to conventional fabric structures, these materials were shown to have higher barrier properties than their unlaminated woven and nonwoven counterparts, or the membrane alone (Branson et al. 1986, Lee and Obendorf 2005). Although microporous membranes and laminates have very low air permeability, their water vapor transmission rate was comparable to most nonwovens (Lee and Obendorf 2005).

2.4 Chemical Properties

Pesticides may contaminate clothing and skin directly during application in the field or by indirect contact with contaminated surfaces. Pesticides may be applied in liquid or granular forms. Thus, clothing and skin contaminants may be liquids (bulk or sprayed forms) or solid dust and soil particles. Chemicals that are considered highly-toxic are commonly produced in granular form to minimize human exposure such as that due to penetration of clothing and skin which is often mediated by liquid flow. These dusts may

accumulate in folds of clothing or other surfaces. Researchers have shown that moisture exposure will generally increase pesticide penetration. Despite granular formulation, elevated temperatures with perspiration and other dermal secretions may have a higher potential to transfer water-soluble pesticides to clothing and skin (Nelson et al. 1993).

Researchers have shown that pesticides can be transferred from clothing with friction (Obendorf et al. 1994, Yang and Li 1993). This is a critical factor when donning and doffing a contaminated garment since even chemicals retained by adsorption that did not initially contact the skin or surroundings may be released to people and their immediate environment. It is also possible for chemicals to accumulate in homes, especially in textiles with large surface areas such as carpets. Residues found as settled dust confirm that chemicals may be redistributed throughout a household that vary with season (Obendorf et al. 2006).

Liquid properties such as surface tension and viscosity play an important role in penetration and may be more influential in penetration than chemical composition of the active ingredient (Lee and Obendorf 2001, 2005, 2007). In commercially produced pesticide formulations, ingredients (adjuvants) which alter the liquid properties of the solution to increase wettability in the target environment are often used in addition to the active ingredient. Due to the highly complex chemical and physical structure of textiles, it is difficult to isolate single factors that determine penetration. However, it is possible to identify predictor variables which combined could attempt to describe the fabric-liquid system. Previous studies have shown that penetration increases with increased viscosity of the challenge liquid. Also, surface tension has a negative relationship with penetration since it is the

difference in surface tension between the liquid and material that causes repellency (Lee and Obendorf 2005).

2.5 Decontamination

Pesticides from the field can accumulate in the home especially in carpeted areas and other textiles with high surface areas (Obendorf et al. 2005). Thus, without successful decontamination, chemicals may accumulate over time and could be transferred to skin or other surfaces by friction (Obendorf et al. 1991, 1994). Decontamination is the removal of chemicals from exposed clothing systems. For textiles, this is most often accomplished by laundering. Removal of pesticide soils is a complex system involving material, chemical and structural factors. Formulation, active ingredients and concentration of pesticides, fiber type, and washing conditions impact effectiveness. Not all fiber types adsorb or release pesticides equally. In the case of contamination by organophosphate pesticides, malathion and methyl parathion, the pesticides are distributed on the surfaces of both cotton and polyester, as well as inside the cotton lumen. One laundering cycle removed most of the surface residue for the cotton and polyester, but was ineffective in removing the soil from the cotton lumen. Although some improvement was observed with repeated washing, removal of pesticide from the lumen continued to be difficult (Obendorf and Solbrig 1986). McQueen et al. (2000) also observed the high adsorptive property of cotton/polyester in comparison to nylon and polyvinyl chloride (PVC) for methomyl, a carbamate pesticide. Although the cotton/polyester fabrics retained more methomyl, these residues were also more readily removed by laundering. Some fabrics such as

nylon and cotton/polyester demonstrate loss of chemical resistance after repeated washing cycles, while others such as PVC retain their properties (McQueen et al. 2000).

Researchers have shown that textile treatments such as renewable starch finish or durable carboxymethylation of cotton increase the amount of pesticide adsorbed by the fabrics. Both treatments also are effective in enhancing the decontamination of cotton fabrics with laundering. Fabric weight also is a critical factor in both adsorption of pesticide and subsequent removal. Heavier materials such as denim retain more chemicals than lighter shirt-weight materials and may release contaminants over time. Thus, finishes that enhance the adsorption and removal of pesticides from lighter weight non-barrier fabrics are potentially useful. The addition of enzymes such as amylase also improves decontamination (Csiszar et al. 1998).

2.6 Self-Decontamination/Detoxification

Not only is protection from initial pesticide exposure in the field a critical factor for protective clothing, but also limiting further contamination when doffing the garment or carrying soiled garments into the home or other environments not directly related to work such as personal automobiles. Self-decontaminating fabric treatments, which decompose pesticides on contact may provide enhanced dermal protection as well as limit garment mediated contamination.

Materials with self-decontaminating treatments are a promising approach to comfortable yet protective clothing systems. This class of materials incorporates compounds with detoxifying properties (such as

oxidation) on to protective textiles. By converting pesticides to potentially less harmful forms on contact, the efficacy of porous materials for limiting dermal pesticide contamination may be enhanced. This project focuses on two such self-decontaminating treatments, N-halamine and metal oxide structures used with a non-barrier, shirt weight plain woven cotton/polyester fabric.

N-Halamines

Organic polymeric compounds with oxidative properties are promising candidates for detoxifying pesticides on protective clothing. N-halamine compounds, which derive their efficacy from disassociation of chloramine bonds (N-Cl) have demonstrated the ability to oxidize commonly used carbamate pesticides which contain sulfur bonds such as aldicarb and methomyl (Fei et al. 2006). Researchers have demonstrated their ability to convert alcohols to ketones, sulfides to sulfoxides and sulfones, and cyanides to carbon dioxide and water (Sun and Xu 1998). They also have biocidal properties (Qian and Sun 2005).

Three forms of chloramine bonds are imide, amide, and amine halamine. The bond stability was found to be inversely related to reaction rate with aldicarb (imide halamine > amide halamine > amine halamine) (Fei et al. 2005, Qian and Sun 2005) as well as biocidal properties (Qian and Sun 2004). The imide bond which is found in 1,3 dimethyol-5,5-dimethylhydantoin (DMDMH) dissociates readily and reacts the fastest with aldicarb compared to the amide and amine bond types (Figure 2.3). Researchers have shown the decrease in aldicarb concentration with exposure to N-halamines and the oxidation of the thio bond to sulfoxide (-SO-) and later sulfone ($-SO_2$). The

formation of these two oxidation products is illustrated in the overall scheme for degradation of aldicarb described in Figure 2.4.

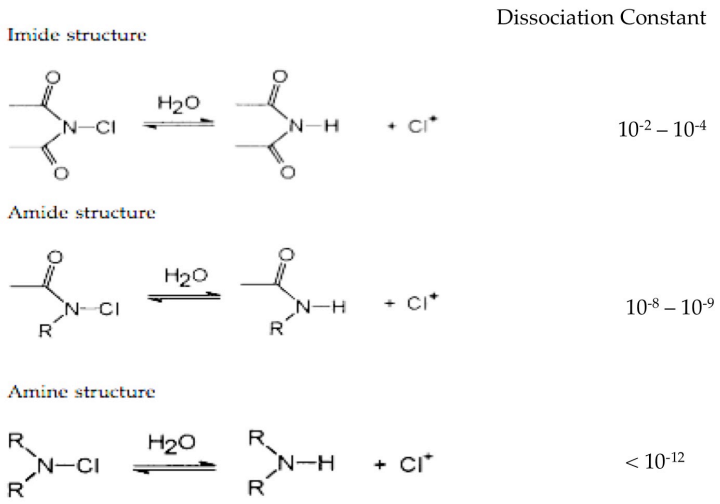


Figure 2.3 Dissociation of N-Cl for N-halamines
(Qian and Sun 2003)

Researchers have developed both imide and amide N-halamine treatments for fabrics; 1,3 dimethylol 5,5-dimethly hydantoin (DMDMH) contains predominantly imide bonds, where as the 3-methylol 2,2,5,5-tetramethyl imidozalidin 4-one (MTMIO) treated fabrics contain amine halamine structures. The imide halamines, though more reactive are significantly less durable than the amines with repeated laundering. Bleaching can reactivate all three types of N-halamines studied. A mixture of highly reactive imide and stable amine compounds may provide the desired properties of both compounds. It is possible that the amine halamines may be

able to recharge the imide halamines on the fabric surface (Qian and Sun 2005).

N-halamine polymers can be grafted onto polyester/cotton and exhibit durable and rechargeable properties when reactivated with a chlorine treatment (Ko et al. 2000, Sun and Xu 1998, Y. Sun and G. Sun. 2001). Higher temperatures contribute to a faster rate of oxidation (Fei et al. 2006), which may make these treatments even more effective for protection from pesticides. Most protective clothing worn by agricultural workers is worn during the summer growing season when temperatures are high.

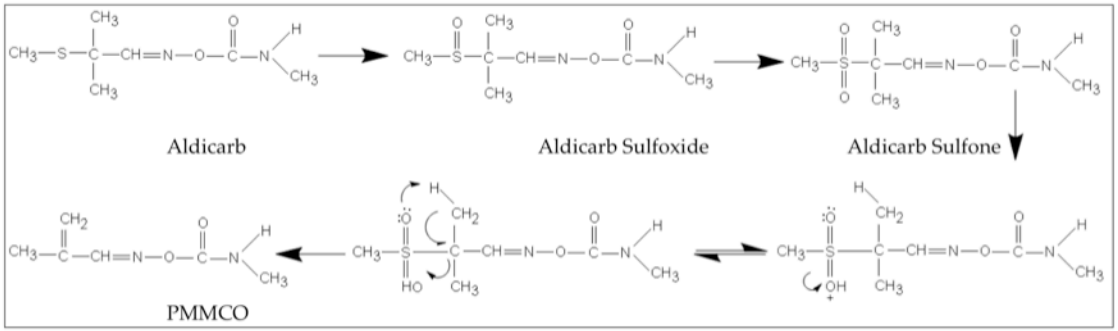
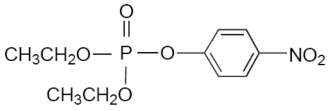


Figure 2.4 Degradation Scheme for Aldicarb (Dixit et al. 2009)

Magnesium Oxide

Inorganic metal oxides such as MgO are known for their high surface reactivity and adsorptive properties. In nanocrystalline form (particle size ≤ 8 nm, aggregate size 3.3 μm) due to polyhedral shapes and high proportion of corner/edge sites there is greater surface area available for reactions compared to typical polycrystalline material. This high surface area combined with high surface reactivity gives these materials great potential for use in decontamination of toxic substances by dissociative chemisorption, or "destructive adsorption" (Klabunde et al. 2002).

Nano-MgO, CaO, and Al_2O_3 have been shown to adsorb polar organics such as aldehydes, alcohols, ketones, and others in very high capacities, substantially outperforming commonly used activated carbon, which physisorbs but does not destructively adsorb (Khaleel et al. 1999). Scientists have incorporated TiO_2 into nonwoven polyester filtration fabrics to aid in degradation of volatile organic compounds (VOC). In this system, the metal oxides act as photocatalysts in the presence of UV light (Park et al. 2006). Dong et al. (2005) treated cotton fabrics with aqueous TiO_2 in a silicone finishing solution to aid in the decomposition of gaseous ammonia also in the presence of UV light. These UV-related "advanced oxidation processes" may also be useful in the outdoor environment. The combination of elevated temperatures during the summer growing season, direct sunlight and moisture may create an effective system for oxidation of pesticides on textile surfaces. This study focuses on nano-MgO because of its high adsorptive properties without the need for activation by UV light exposure.



Paraoxon

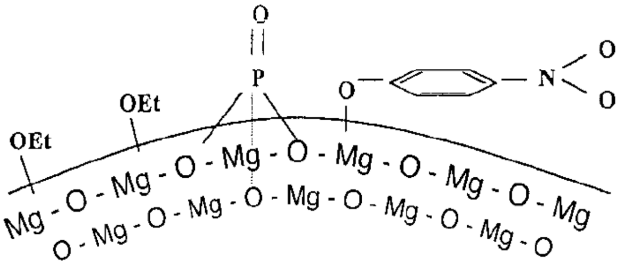


Figure 2.5 Destructive Adsorption of organophosphate compound (paraoxon) by MgO (Klabunde 2002)

Klabunde et al. (2002) found that nanocrystalline MgO reacts faster and in higher capacity than activated carbon, a commonly used material for chemical and military protective clothing. Unlike activated carbon, which only physisorbs, MgO is able to immobilize organophosphate compounds by cleavage of P-O and P-F bonds, illustrated in Figure 2.5. In the experiment that follows, MgO was tested both alone and with starch in order to combine properties of physical and destructive adsorption.

CHAPTER THREE: EXPERIMENTAL PROCEDURES

The experiments were designed to focus on the mechanism of destructive adsorption of the challenge pesticide (aldicarb) by conventional woven fabrics treated with self-decontaminating and adsorbent finishes. N-halamine and MgO were chosen for their chemical reactivity, whereas starch was chosen for its ability to physically adsorb and possibly aid in the removal of contaminants by laundering (Csiszar et al. 1997). A comparative study for untreated, starch, N-halamine, MgO/starch, and MgO was conducted at a low contamination load to focus on the fabric mechanism without penetration or repellency. Then the MgO/starch treatment was chosen for a variable load study at three higher contamination levels.

3.1 Materials

Fabric Selection and Treatments

Cotton/polyester plain-woven fabric is used in long-sleeved shirts commonly worn by agricultural workers. These types of fabrics generally demonstrate good adsorptive properties, relative ease of decontamination by laundering, popular usage by workers, and relatively low cost. Previous studies have demonstrated the adsorptive properties of these fabrics in relation to chemical protection. In a laundering study, cotton/polyester fabrics adsorbed higher amounts of contaminant (carbamate pesticide, methomyl), yet these residues were also more readily removed in comparison to nylon and PVC fabrics (McQueen et al 2000). In this study 35% cotton/65% polyester plain weave textiles (Testfabrics, West Chester PA) were used.

N-Halamines

Since the imide structure is more effective in initially oxidizing aldicarb, this form was chosen to represent the N-Halamine class of compounds in this study. 4% DMDMH (1,3 dimethylol 5,5-dimethly hydantoin) treated 35% cotton/65% polyester plain weave textiles (Testfabrics, West Chester PA, G. Sun research group, UC Davis CA) were activated by submersion in diluted chlorine bleach solution (50 water:1 bleach by volume) for 30 min. Then, samples were rinsed with de-ionized water and air dried in a drying cabinet.

Magnesium Oxide Nano-particles and Starch Treatments

Magnesium oxide (crystallite size ≤ 8nm, specific surface area ≥ 230 m^2/g) (Nanoscale Materials Inc., Manhattan KS) and starch were applied to 35% cotton/65% polyester plain weave fabrics by saturating the fabrics by dipping into in an aqueous slurry, then removing excess liquid using a padder, followed by drying in a conditioned room at 25 °C, 65% RH. There were three different slurries, 3% MgO, 3% starch, and a mixture of 3% MgO/starch by weight in HPLC grade water. Dry fabrics (conditioned for 24 h) were weighed before and after application of nanoparticles and starch. Weight percent finish contexts were as follows: MgO 3.7%, MgO/starch 3.6%, starch 2.5%.

All fabrics, including the untreated 35% cotton/65% polyester plain weave were placed in a conditioned room (25°C, 65% RH) for 24 h prior to testing.

Collector Layers

The silicone elastomer membrane (PharmElast, SF Medical, Trelleborg Sealing Solutions, Hudson MA) was chosen as a collector layer for both repellency and penetration to replace adsorbent paper (used in the standard method ASTM 2130) due to observed oxidation of the pesticide on the paper layer alone due to high surface area and contact with air. Obendorf et al. (2003) had successfully modeled skin using a silicone elastomer membrane sandwiched between two layers of cellulose acetate. Their method studied penetration with a Franz diffusion cell with collection fluid below the fabric and model skin layers. So the model skin served as a semi-permeable layer for the pesticide to diffuse through over time rather than as a collector.

The elastomer membrane created an extra peak at 1.9 min retention time in HPLC analysis. Thus, the membranes were extracted with successive rinses in a 1:1 by volume water and acetone mixture followed by water until no peaks were observed. The resulting material no longer had the original powder coating and had a stickier consistency.

Challenge Pesticide

The model pesticide included in this study is aldicarb, (2-methyl-2(methylthio)propanal o-[(methylamino)-carbonyl] oxime). This carbamate ester has been manufactured since 1965 and is distributed under the trade name Temik®. It is commonly applied to the soil for a wide range of plants to control certain insects, mites, and nematodes. Aldicarb has a high potential for absorption through skin and gastrointestinal tract (Maibach et al. 1971). For this reason, it is produced commercially in a granular formulation. The Environmental Protection Agency has classified aldicarb in its highest toxicity

category (Ragoucy-Sengler et al. 2000).

Aldicarb is susceptible to oxidation and hydrolysis. Its two primary oxidation products are aldicarb sulfoxide and aldicarb sulfone (aldoxycarb). Conversion to sulfoxide occurs relatively rapidly, 48% of the parent compound is oxidized to the sulfoxide form within 7 days in soil and can even be observed by simple exposure of a solution with air. The second oxidized product, aldicarb sulfone, does not occur as quickly. Both metabolites are considered toxic (IPCS 1991). It is detoxified via hydrolysis to oximes and nitriles. This scheme is shown in Figure 2.4, aldicarb is converted to aldicarb sulfoxide, aldicarb sulfone, and 2-propenal, 2-methyl-, O-[(methylamino)carbonyl]oxime (PMMCO).

3.2 Method Development

Relevant properties for evaluating protective fabric properties include; permeation, penetration (flow through the material), repellency (challenge does not penetrate past the surface), and absorption/adsorption (retention within or in proximity to the material structure). There are three major methods for contamination of fabrics based on modeling different target conditions. The gutter test (EN 368/ISO 6350), used to test Type 6 PPE garments in Europe, models an accidental splash or spill. The atomizer method (BBA 3-3/2), developed in Germany, simulates field-spraying contamination. The pipette method (ASTM F 2130-01), used in the United States, was developed to focus on performance with a splash or spill with known volumes of liquid pesticides. The model method used in this study is based on this ASTM F 2130-01 standard method for measuring repellency, retention, and penetration of liquid pesticide formulation through protective

clothing materials (Shaw et al. 2000). There are several noted adaptations to minimize the effect of bulk flow of the liquid through the fabric and maximize liquid/fabric surface area contact while still simulating a liquid droplet contaminant.

In the standard method, the test material placed on top of a collector layer is exposed to the chemical challenge solution via pipette from a fixed height of 12 cm. Then, after 10 min another collector layer is placed on top to measure repellency. Each of the three fabrics is then extracted separately in solution and chemical concentration determined via gas (GC) or high performance liquid chromatography (HPLC). This procedure is illustrated in Figure 3.1.

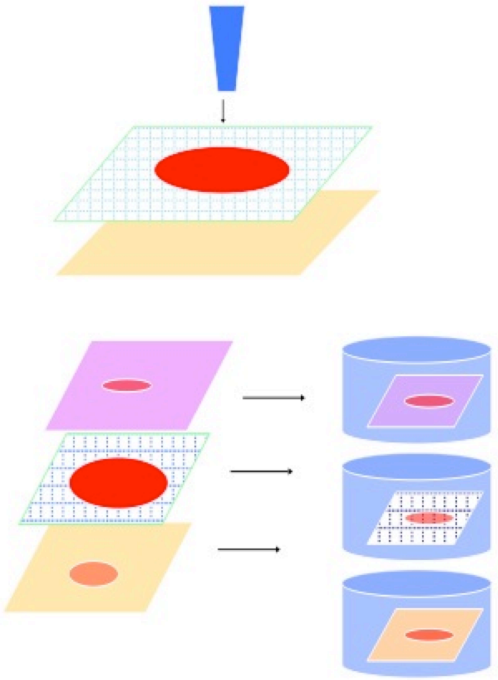


Figure 3.1 Contamination by single pipette and extraction of fabric and membrane layers (ASTM Method 2130)

The standard test was developed to compare fabrics with different structures and surface/pore characteristics so a measurement of concentration

of any chemical contaminant on each layer was appropriate. However, when testing with self-decontamination treatments on a single fabric type, the relevant observations for this study include the creation (and identification) of several possible degradation products and their relative concentrations represented by individual chromatographic peak areas. The standard method uses an absorbent paper layer for both repellency and penetration collector materials. Preliminary results, however, demonstrated increased formation of oxidized products of aldicarb on this paper layer due to the large surface area of the paper fibers and exposure to air. In this testing system, the paper layers were replaced by an elastomeric silicone membrane to minimize oxidation of the pesticide on the collector material and to more reasonably model human skin (Obendorf et al. 2003). Acetonitrile, methanol: water (60:40) and water were tested as potential extraction solvents for aldicarb. Since there was little difference in effectiveness, water (HPLC grade) was chosen.

The single 100 μL droplet of challenge liquid pipetted from 3 cm above the fabric covered an area less than one quarter of the total 10 cm^2 area. The specimen size for both the test fabric and collector layers was reduced to 2.5 cm squares. This allowed for a reduction in extract solution volume to 10 mL as well as elimination of the evaporation step to concentrate the solution for analysis. The single drop liquid contamination delivery method was also changed to multiple drop delivery, in order to minimize the effect of bulk liquid flow through the fabric and more closely model contamination by small droplets or accumulated spray residue.

3.3 Final Experimental Method

The final method used in this study was as follows (Figure 3.2): samples of chlorinated N-halamine, metal oxide and blank fabrics were cut into 3 x 3 cm squares. Each sample was placed on a silicone elastomer collector layer (also 3 x 3 cm square) supported on a Plexiglas plate. Fabrics were contaminated by 9 drops of aqueous aldicarb solution in a square pattern containing 3 rows of 3 drops each spaced 0.5 cm apart delivered by a multipipettor (Transferpette-8, BrandTech, Essex CT) from a 1.0 cm height. Volumes of challenge solution were varied in each experimental section. After 10 min, a second collector layer of equal size covered the test fabric/collector assembly for 2 min. Each of the three layers was then placed separately into jars containing 10 mL of HPLC grade water. These jars were shaken at 200 rpm for 1 h. Extract liquids containing MgO were filtered with a nylon syringe filter (30 mm, 0.45 μm, Alltech Assoc. Inc. Deerfield IL). Aliquots of 1mL were removed from each jar and analyzed by HPLC (Agilent 1100, Santa Clara CA). Samples were tested in replicates of three. These modifications to the standard method reduced procedure time; minimized error possibly introduced by the evaporation step and long waiting time between extraction and analysis, as well as reduced chemical waste.

Since the model pesticide, aldicarb, is degraded at temperatures above 40°C, analysis by high performance liquid chromatography (HPLC) which is effective at lower temperatures was used with the following conditions: 15 ˚C, C18 column, the mobile phase was a mixture of 40% acetonitrile with 60% H_3PO_4/water buffer (pH 3), 220/4 nm UV detector, flow rate 1 mL/min, with detection for 12 min.

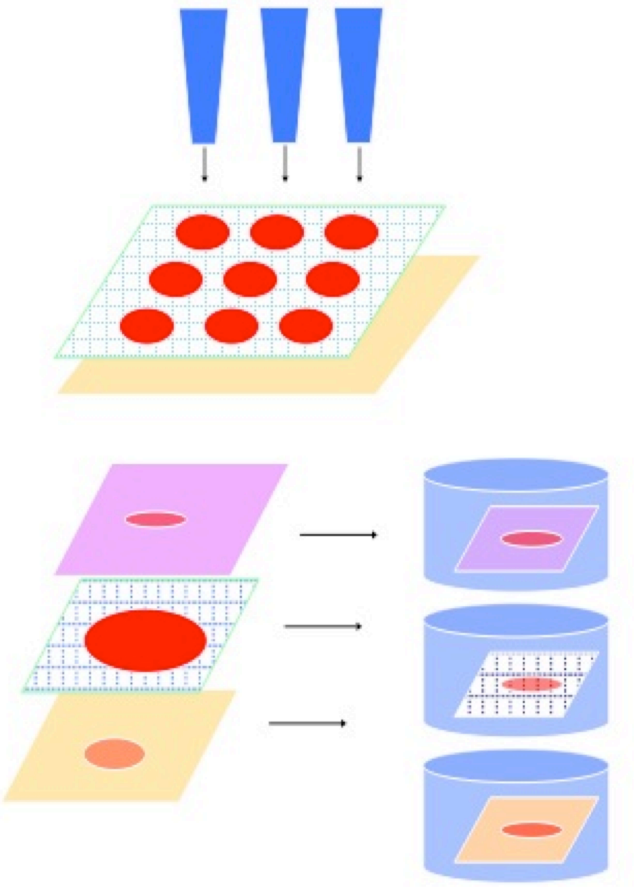


Figure 3.2 Contamination by multiple pipettor and extraction of fabric and membrane layers

Since bulk liquid flow through porous media is a dominant mechanism for chemical penetration through a woven fabric, a low liquid challenge load (36 µL total) was used initially to maximize adsorption without penetration through the fabrics. In the low load study (36 µL), five different textile treatment conditions were used; 4% DMDMH, MgO, MgO/starch, starch and untreated (control). They were contaminated by a total of 36 µL $7.5x10^{-3}$ M aqueous aldicarb (0.27 µmol) delivered in a 3 x 3 (4 µL) drop formation delivered by multiple pipettor in 3 rows.

A load study was then conducted for the MgO/starch treated fabrics (with challenge loads of 90 μL (0.70 μmol), 135 μL (1.04 μmol), and 180 μL (1.39 μmol). The challenge solution is $7.5x10^{-3}$ M aqueous aldicarb delivered in a 3 x 3 (10, 15, 20 μL) drop formation delivered by multiple pipettor in 3 rows. The extraction method was consistent for all load level conditions.

Peaks of Interest

Aldicarb appeared at a retention time of 4.0 -4.2 min. Aldicarb sulfoxide was located at approximately 2.1 - 2.3 min. Aldicarb sulfone (aldoxycarb) produced a major peak at approximately 2.5 – 2.8 min. Aldicarb and its products, sulfoxide and sulfone were identified by comparison to known standards (ChemService, West Chester PA). These peaks produced by mixing known standard compounds can be seen in Figure 3.3. A third oxidized product appeared at 3.4 – 3.6 min. This product was identified by Dixit et al. (2009) as 2-propenal, 2-methyl-, O-[(methylamino)carbonyl]oxime (PMMCO) using LC/MS/MS. These peaks can been seen in Figure 3.4, a chromatograph of an extracted MgO-treated fabric layer after contamination with aldicarb. Standard curves were created using known quantities of aldicarb, aldicarb sulfone and sulfoxide (Figures 3.5, 3.6).

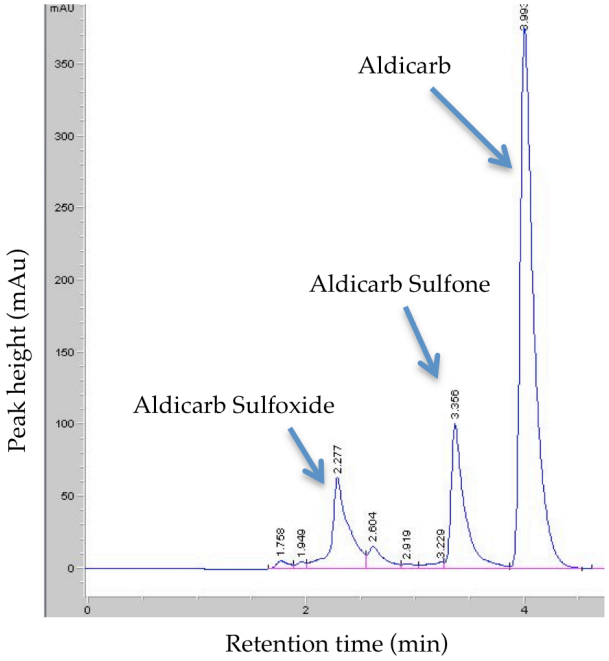


Figure 3.3 Identification of aldicarb, aldicarb sulfoxide and sulfone by HPLC prepared by mixing known standard compounds

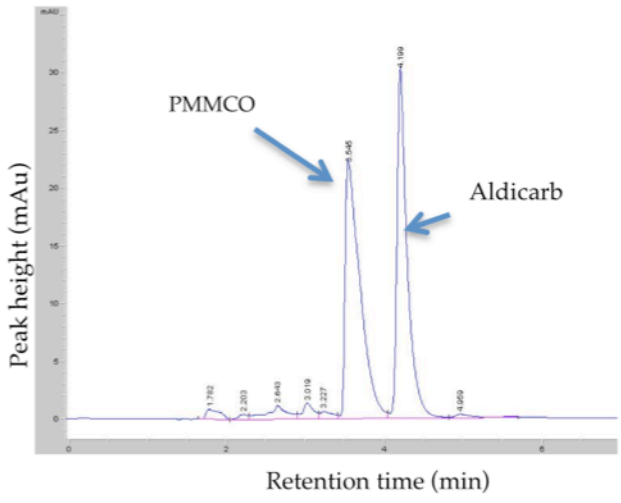


Figure 3.4: HPLC Chromatogram for MgO treated fabric sample showing peaks for PMMCO and aldicarb

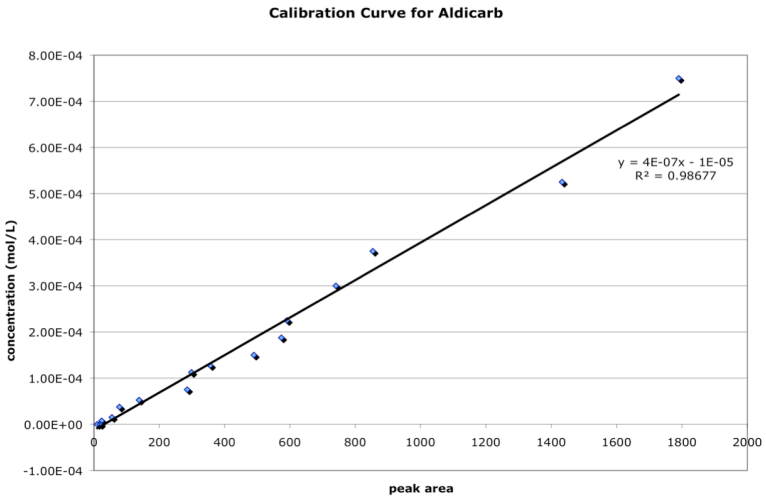


Figure 3.5 Calibration curve for aldicarb

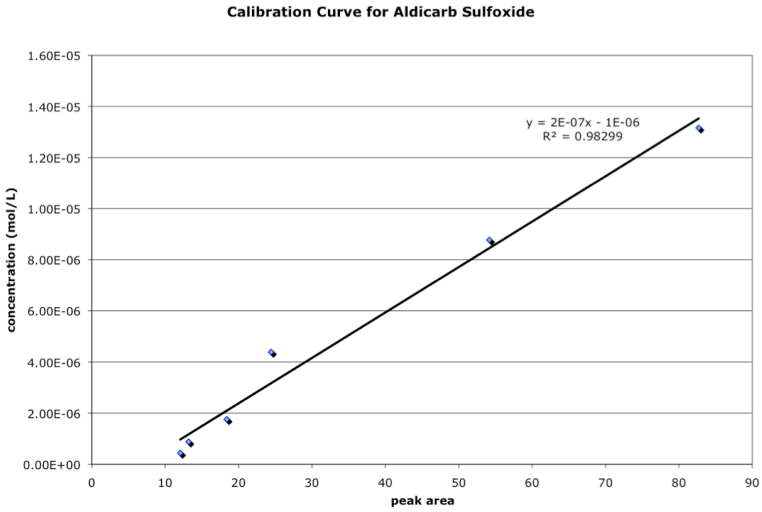


Figure 3.6 Calibration curve for aldicarb sulfoxide

3.2.1 Evaluation of Methods

The objective of this study was to determine whether the addition of self-decontaminating surface treatments could add protection from pesticide on traditional woven fabrics. A modified contamination and extraction method based on ASTM Standard Method 2130 was developed.

The fabric extraction was conducted in a relatively low volume (10 mL) HPLC grade water. This made the concentrations high enough to eliminate the step involving concentration by evaporation and then bringing samples up to 2 mL volume, which was used in preliminary testing. However, not all of the challenge contaminant was extracted during the process. For example, when contaminated with 36 μL, the control fabric showed 13 μmol (standard deviation 0.05 μmol) μmoles of aldicarb extracted while the total theoretical amount applied was 27 μmol. Considering this large difference between amounts applied and extracted, it was not possible to determine a total molar mass balance for the sample set.

A collector layer that is less cumbersome than both the elastomer membrane and the absorbent paper may be preferable. For future experiments it may be beneficial to use a different collector layer that is thinner, yet adsorbent without contributing to increased oxidation.

Assumptions and Limitations

Fabric samples were assumed to be from a uniform and normally distributed selection of yardage. Durability of nanoparticle or starch treatments was not included in this study. Each compound was identified by one major peak value at a given retention time. In some cases other very small

peaks were found, noted but only peaks with heights greater than 1.0 mAu were included in statistical analysis.

Statistical Analysis

Samples were compared using Student's t-test for two sample means. This method tests the null hypothesis that the means for two samples with equal variance and which are from a normally distributed population are equal. A threshold value $\alpha = 0.05$ was used to determine whether the means were significantly different within a 95% confidence level. If the probability (p-value) is less than $\alpha = 0.05$, the means are significantly different for the given samples. For the experiments evaluated in both the low load and variable load studies, the sample size (n=3) was small. It would have been preferable to have a larger sample size to minimize variation within each set.

CHAPTER FOUR: RESULTS AND DISCUSSION

The range of contamination volumes for both low load and multiple load studies were chosen to minimize penetration and repellency in order to focus on the mechanism of destructive adsorption of aldicarb on the fabric layer. Both N-halamine and MgO treatments demonstrated an ability to convert aldicarb to one or more of its oxidized products.

4.1 Comparison of Fabric Treatments

The total contamination load was 0.27 μmol of aldicarb, based on the control sample, 48% of this was recovered from the fabric by the extraction method used (of the applied 0.27 μmol of aldicarb, 0.13 μmol were recovered from the untreated fabric according to the standard curve ($y = 45x10^{-7} x - 1 x10^{-5}$, $R^2 = 0.99$). Due to the low percentage of chemical recovered by this extraction method, a qualitative identification of compounds of interest was primarily used since it is not possible to do a mass balance. Since a known standard for the third oxidized product, PMMCO was unavailable to create a calibration curve, it was not possible to determine molar quantities of this product. A compound believed to be a contaminant was found at 5.3 min in many samples and not analyzed.

No evidence of penetration or repellency was found for any of the fabrics at this contamination level indicated by an absence of peaks in the chromatographs from the extracted upper and lower membrane layers. This is demonstrated in Figure 4.1, which shows a representative sample of chromatographs from the three extracted material layers for the sample

treated with MgO/starch. In this sample, the only significant peaks are due to the presence of aldicarb and PMMCO in the fabric layer. Figure 4.2 provides a comparative view of the extracted fabric layers from all of the samples contaminated at the 36 µL, 0.27 µmol load level. These data are summarized in Table 4.1, which shows mean peak areas for each chemical detected with standard deviation in parentheses.

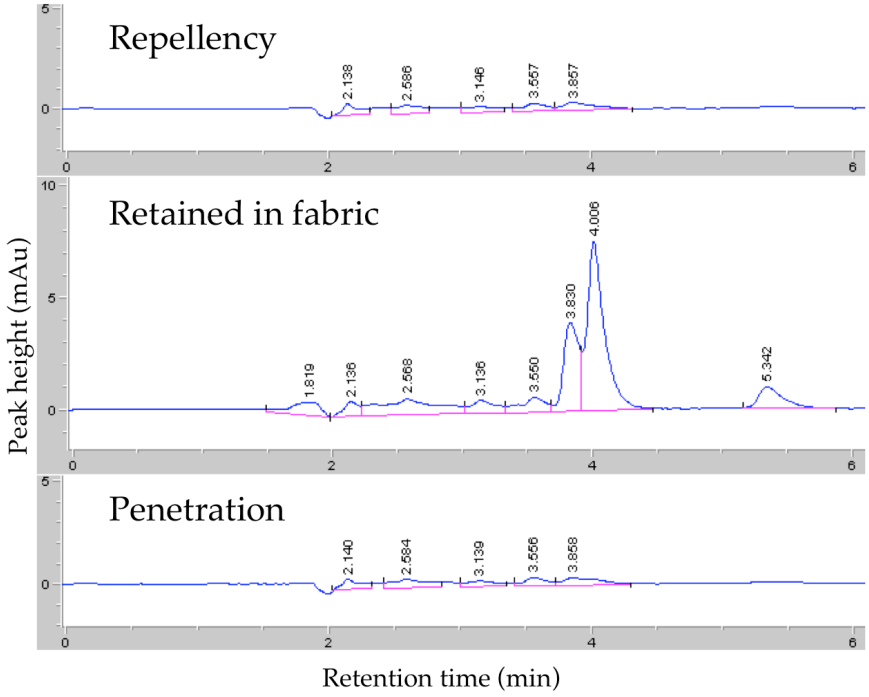


Figure 4.1: MgO/starch treated fabric contaminated with 35 µL (0.27 µmol) aqueous aldicarb

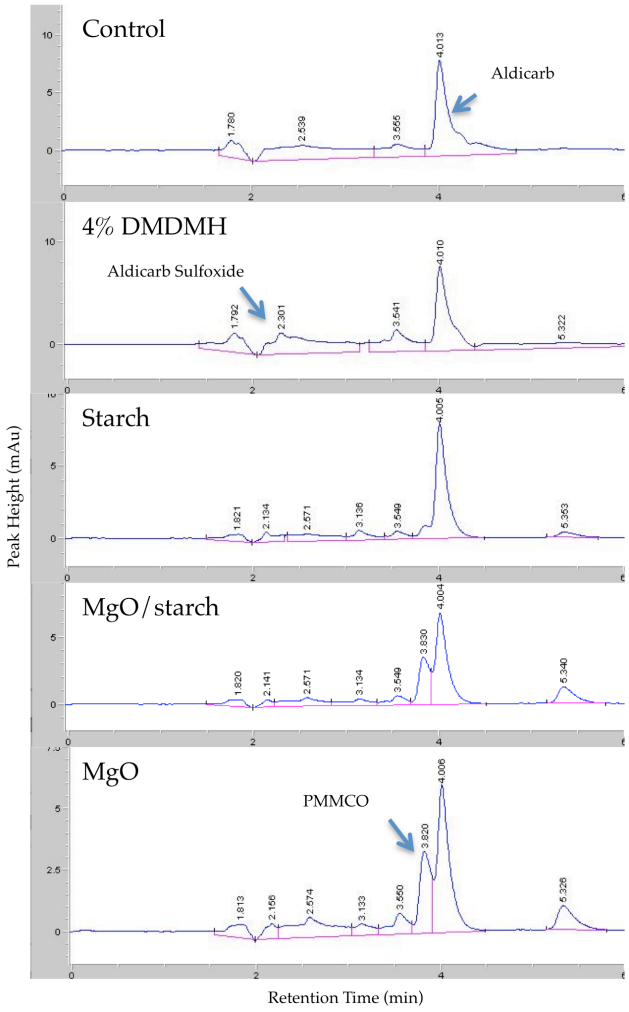


Figure 4.2: HPLC Analysis of fabric layers contaminated with 36 µL (0.27 µmol) aqueous aldicarb

Table 4.1: Presence of Chemicals[4] in Fabric Layers Contaminated with Aldicarb at Low Load (36 µL, 0.27 µmol)

	Aldicarb (peak area mAu^2)	Aldicarb Sulfoxide (peak area mAu^2)	PMMCO (peak area mAu^2)
Control	82 (12)	ND	ND
4% DMDMH	80 (3)	32 (1)	ND
Starch	77 (2)	ND	ND
MgO/Starch	69 (4)	ND	23 (3)
MgO	60 (2)	ND	12 (2)

[4] Peak Areas determined by HPLC (mAu), standard deviation in parentheses, ND means not detected

Aldicarb was found in all fabric layers. The control and starch treated fabrics showed similar results, aldicarb being adsorbed into the fabric with no observed degradation. Aldicarb sulfone was not detected for any of the fabric treatment conditions.

The quantities of aldicarb (µmol) extracted from the fabric layers are summarized in Table 4.2 and Figure 4.3. These values were determined by using the standard curve ($y = 45x10^{-7} x - 1 x10^{-5}$, $R^2 = 0.99$). These data highlight the difference in destructive adsorption alone, in the case of the MgO treated fabric, in comparison to this mechanism combined with physical adsorption derived from starch in which aldicarb was retained in the fabric without degradation.

Table 4.2: Aldicarb in Treated Fabric Layers Contaminated at Low Load (36 µL, 0.27 µmol)

	Mean (µmol)	Standard deviation (µmol)
Control	0.13	0.05
4% DMDMH	0.12	0.01
Starch	0.11	0.01
MgO	0.04	0.01
MgO/Starch	0.08	0.02

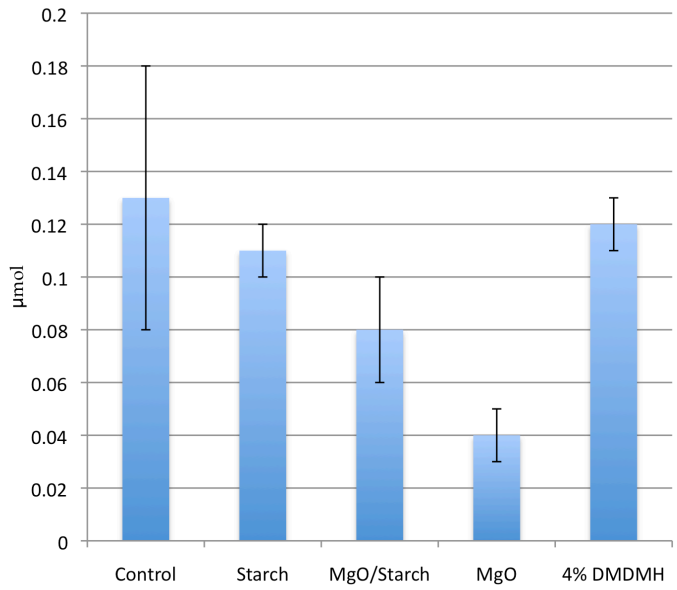


Figure 4.3: Aldicarb retained in fabric layers at low contamination load (36 µL, 0.27 µmol)

Quantities of aldicarb for each test condition were compared using a two-tailed t-test assuming equal variance, $\alpha = 0.05$. The results are summarized in Table 4.3, probabilities less than $\alpha = 0.05$ are highlighted in bold. The MgO treated fabric was the only treatment found to be significantly different from the untreated control fabric, however the control samples also had the largest standard deviation (0.05). MgO treated was the only test case to significantly differ from all other treated samples.

Table 4.3: Probabilities for t-tests of Aldicarb in Treated Fabric Layer Contaminated at Low Load (36 μL, 0.27 μmol)

	Control	4% DMDMH	Starch	MgO	MgO/Starch
Control		0.745	0.523	**0.041**	0.155
4% DMDMH			0.323	**0.001**	**0.023**
Starch				**0.024**	**0.032**
MgO					**0.024**

The first oxidized product, aldicarb sulfoxide (degradation scheme shown in Figure 2.4) indicated by a peak between 2.1 – 2.3 minute retention time was found only in the extracted fabric layer treated with the N-halamine 4% DMDMH. According to calculations using the standard curve ($y = 2 \times 10^{-7}X - 1 \times 10^{-6}$ $R^2 = 0.98$, shown in Figure 3.6) there were 0.05 μmol (st. dev. 0.0016) of aldicarb sulfoxide present. There was no evidence of the second

oxidized product, aldicarb sulfone for any of the treatments. However, the third oxidized product, PMMCO, was found in both the MgO and MgO/starch treated materials. This suggests that at these concentrations, MgO is a more powerful self-decontaminating treatment than the N-halamine.

4.2 Comparison of Effectiveness of MgO/starch Treatment at Various Contamination Levels

Where possible, molar quantities were determined using a standard curve. In some cases however, although the chemical was detected, it was outside of the calculable range for the standard curve. Table 4.4 shows the relative peak areas for aldicarb and its oxidized products in the MgO/Starch treated fabric layer. No significant repellency or penetration was found at these load levels (Figures 4.4, 4.5, 4.6). Aldicarb was the only chemical detected in the control samples (Figure 4.2).

Table 4.4: Presence of Chemicals in MgO /Starch Treated Fabric Layers Contaminated with Aldicarb at Variable Load (90 - 180 μL)

Contamination Load	Aldicarb (peak areas mAu)	Aldicarb Sulfone (peak areas mAu)	PMMCO (peak areas mAu)
90 μL	175 (2)	21 (2)	409 (80)
135 μL	279 (8)	22 (2)	333 (46)
180 μL	245 (6)	23 (2)	396 (82)

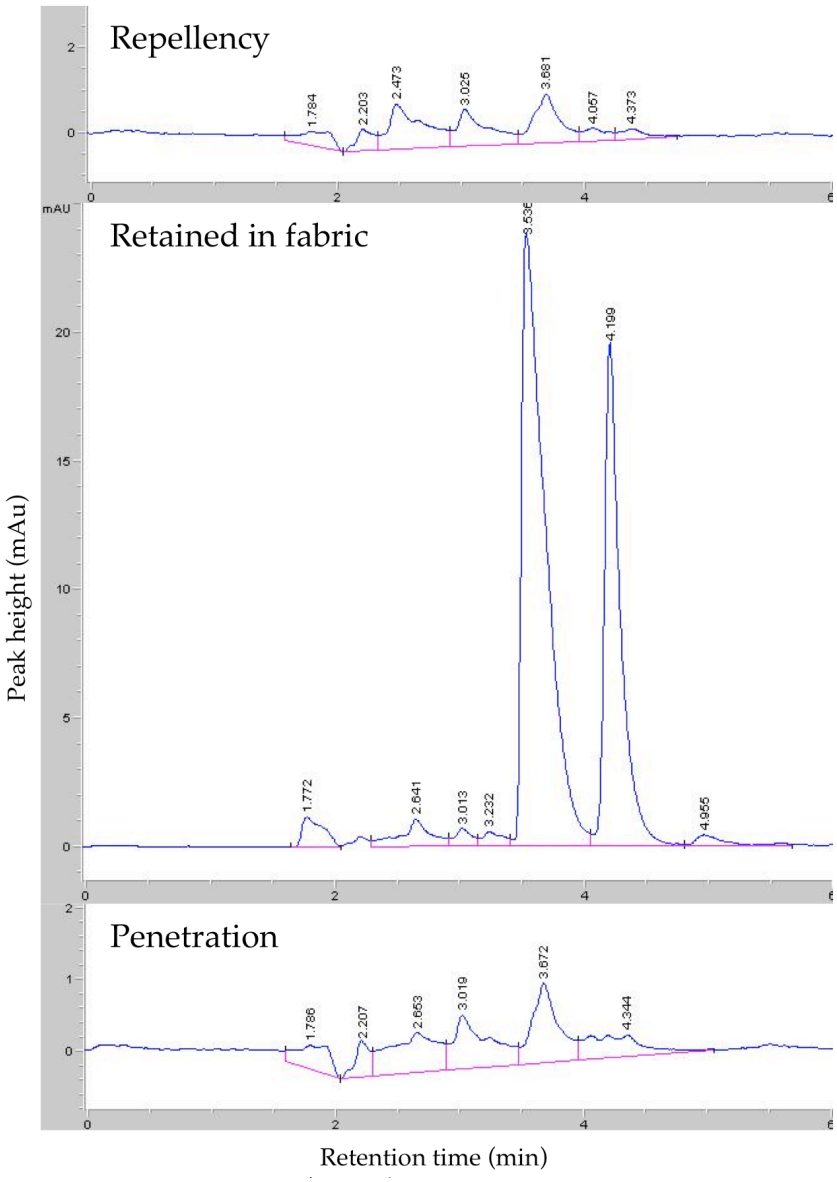


Figure 4.4: MgO/starch treated fabric contaminated with 90 µL (0.70 µmol) aqueous aldicarb

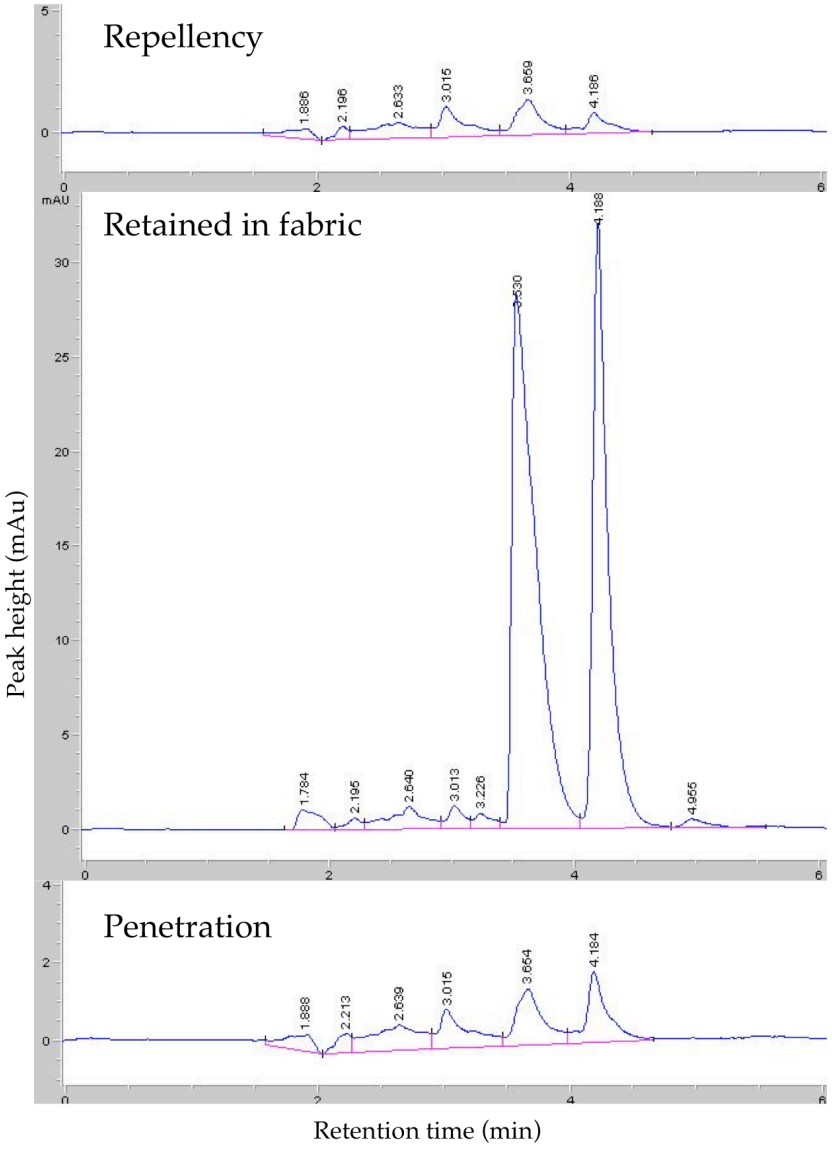


Figure 4.5: MgO/starch treated fabric contaminated with 135 µL (1.04 µmol) aqueous aldicarb

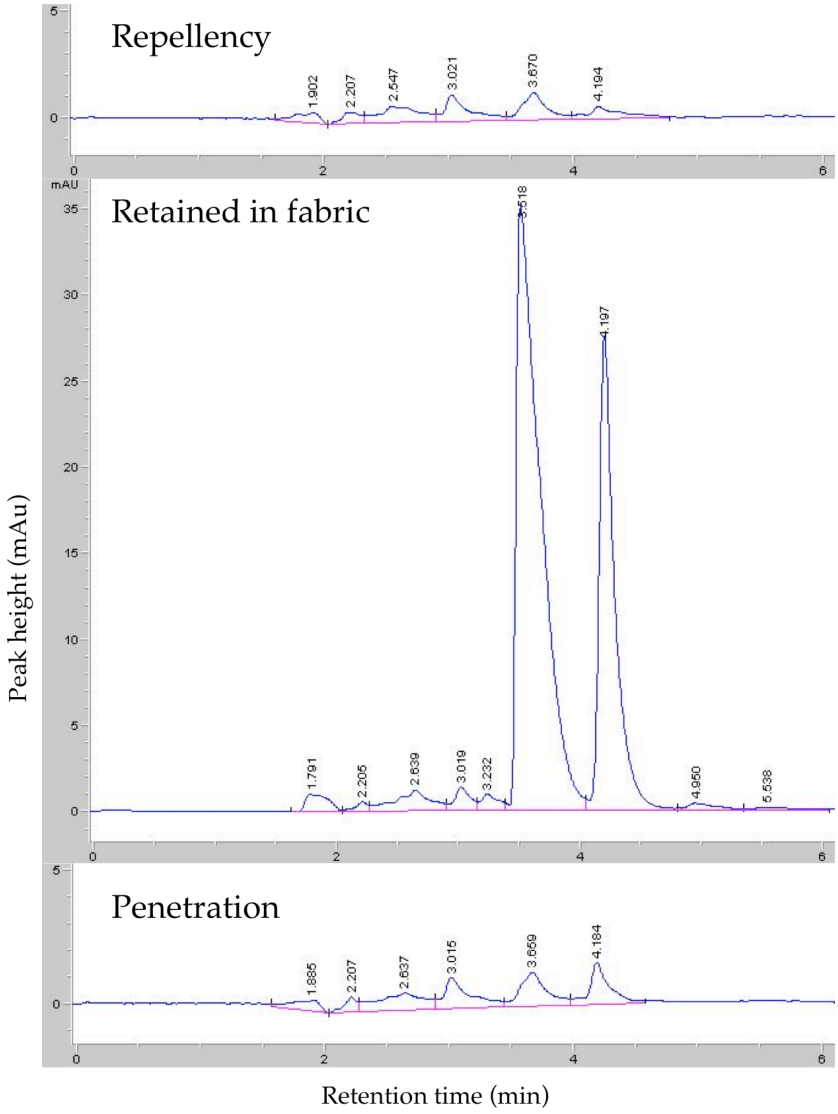


Figure 4.6: MgO/starch treated fabric contaminated with 180 µL (1.39 µmol) aqueous aldicarb

Quantities of aldicarb found in the fabric layers were determined using a standard curve ($y = 4 \times 10^{-7}X - 2 \times 10^{-5}$ $R^2 = 0.99$, Figure 3.5). These values (with standard deviation in parentheses) are summarized for control and MgO/Starch treated samples in Table 4.5. Quantities of aldicarb for control and MgO/starch samples were compared using a two-tailed t-test assuming equal variance, $\alpha = 0.05$. For the two higher contamination levels, 135 μL (1.04 μmol) and 180 μL (1.39 μmol), the quantities of aldicarb were significantly different with p-values of 0.042 and 0.003 respectively. The 90 μL (0.70 μmol) load value had a p-value of 0.13. When the samples were compared to each other across load levels they were confirmed to be significantly different (Table 4.6).

Table 4.5: Presence of Aldicarb in Control and Starch/MgO Treated Fabric Layers Contaminated with Aldicarb at Variable Load (90, 135, 180 μL)

Contamination Load	Control (μmol)	MgO/Starch (μmol)
90 μL	0.58 (0.01)	0.60 (0.01)
135 μL	0.93 (0.03)	1.01 (0.03)
180 μL	1.20 (0.03)	0.78 (0.02)

Where possible molar quantities were determined by calculation with standard curve (aldicarb $y = 4x10^{-7} x - 2x 10^{-5}$ $R^2 = 0.99$, aldicarb sulfone $y = 3x10^{-7} x - 3x10^{-7}$ $R^2 = 0.83$). In some cases aldicarb was detected, but the concentration was out of the range for calculation with the standard curve. Aldicarb sulfoxide was not detected. Since it was not possible to create a standard curve for PMMCO, peak areas were used for comparison of relative abundance.

Table 4.6: Probabilities for Aldicarb in Fabric Layers Contaminated at Variable Load (90, 135, 180 μL)

	Control 135 μL	Control 180 μL	MgO/ Starch 90 μL	MgO/ Starch 135 μL	MgO/ Starch 180 μL
Control 90 μL	0.000	0.000	0.131	0.000	0.000
Control 135 μL		0.001	0.000	0.041	0.003
Control 180 μL			0.000	0.003	0.003
MgO/ Starch 90 μL				0.000	0.000
MgO/ Starch 135 μL					0.001

At all three contamination levels, aldicarb, aldicarb sulfone and PMMCO were found in the MgO/starch treated fabric layer (Figures 4.4, 4.5, 4.6). The first oxidized product, aldicarb sulfoxide was not detected. This is consistent with the degradation scheme (Figure 2.4) and previous studies that show this product to more rapidly convert to the more stable aldicarb sulfone (Bartley et al. 1970). These findings confirm that destructive adsorption has occurred in the treated fabric layers.

CHAPTER 5: CONCLUSIONS

The objective of this study, to develop a working model system for studying adsorption with self-decontaminating surface treatments on traditional work clothing material, was achieved by modification of the standard ASTM test method 2130. The relatively low contamination volumes produced neither penetration nor repellency, which made it possible to focus on the mechanism of adsorption. Results presented in this study were consistent with known schemes for the degradation of aldicarb (Figure 2.4).

Destructive adsorption was observed for textiles treated with MgO. Physical adsorption was also enhanced with the addition of starch. Some degree of degradation was observed for textiles treated with N-halamine. However, the treatments including MgO nanoparticles were able to further decompose aldicarb to the third oxidation product, PMMCO. This is consistent with the degradation pathway observed with TiO_2 (Woo and Obendorf in preparation). However, this compound retains the N-methylcarbomoyl group, which is also expected to be toxic (Dixit et al. 2009). The issue of possible continued toxicity even with degradation of the pesticide on the garment surface emphasizes the importance of these self-decontaminating treatments and others like them as part of a multi-mechanism protective garment system that combines both material and functional design characteristics. Recommendations for future work may include a laundry study to determine if these finishes enhance overall decontamination. The possibility of incorporating MgO nanoparticles into a durable finish may also be beneficial. Further tests with other common classes of pesticides such as organophosphates would also be useful.

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